

Research Letter

Reflection Band Control of Inverse Opal Film with Photoresponse Properties of Push-Pull Type Azobenzene LC Polymers

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DcAz2Mc and DR1Mc molecules having push-pull type of azobenzene groups are synthesized, and their photo-orientational behaviors are investigated in the polymer system. In order to understand the relationship between a molecular structure and its physical properties, electronic structure calculation is computationally carried out. Regarding to their photo response properties, the copolymers of *poly*(DcAz2Mc-co-M6PBMe) and *poly*(DR1Mc-co-M6PBMe) are infiltrated into inverse opal films, and Bragg reflection shifts are observed under photostimuli. When the linearly polarized light is irradiated, Bragg reflection bands are shifted to the longer wavelength region as reflective index increases.

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1. INTRODUCTION

Recently, in the fields of telecommunication and optical industry, a way to tailor the propagation of light has attracted considerable attention for high-speed and wide-bandwidth information processing. Photonic crystals (PCs) having a three-dimensionally (3D) ordered structure with a periodicity in the optical wavelength range have been proposed as a feasible material to confine light, to guide light, or to inhibit or amplify spontaneous emission properties [1, 2]. The self-assembly method is simple and cost-effective method for fabricating 3D PCs such as an opal structure consisting of colloidal spheres and air voids. In addition, an inverse opal structure can be prepared by using the opal structure as template. With the opal and inverse opal structures, a photonic bandgap (PBG), providing a wavelength range of forbidden propagation in all directions, can be realized. It is known that the PBG mainly depends on the periodicity of spheres and the refractive indices of components, as can be expressed by the following Bragg's equation:

$$\lambda = 2\sqrt{\frac{2}{3}}d\sqrt{n_a^2f + n_b^2(1-f)}, \quad (1)$$

where λ is the wavelength of the Bragg reflection under normal incident condition, d is the distance of periodic units in dielectrics, f is the volume fraction of dielectrics, n_a and n_b are refractive indices of dielectrics. Therefore, a change in either spacing or refractive index is expected to cause a shift of the Bragg reflection band. There are many studies for control of Bragg reflection band by incorporation of low-molecular-weight liquid crystals (LMWLCs) in the inverse opal system, because LMWLCs have a large optical anisotropy, and consequently change in the refractive index can be induced through the change in molecular orientation by applying electric field or photoreaction [3].

On the other hand, we reported that the photochemical switching of Bragg reflection band of a silica inverse opal structure infiltrated with polymer LC bearing azobenzene chromophores. In our previous works [4–7], stable and reversible shift of Bragg reflection band was achieved by irradiation of linearly and circularly polarized light, causing the change in the birefringence through the reversible transformation of azobenzene chromophores between uniaxial and random states. However, the response time was slow. The response property is closely related not only to less response property of polymeric materials, but also to the

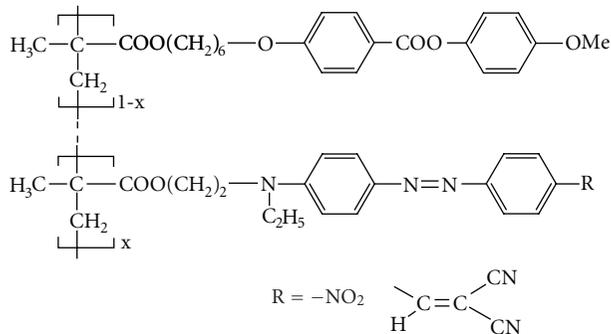


FIGURE 1: Molecular structures of *poly*(DR1Mc-*co*-M6PBMe) and *poly*(DcAz2Mc-*co*-M6PBMe) containing nitro- and dicyano-end groups, respectively. ($x = 1, 0.05$).

electronic property of azobenzene dyes. It is well known that electronically push-pull type azobenzene dyes show better photoalignment property compared with nonpush-pull type azobenzene dyes. Therefore, in this study, we synthesized two kinds of push-pull type azobenzene dyes, DcAz2Mc and DR1Mc, and explored their photoresponse properties experimentally and theoretically. In addition, Bragg reflection band shift was investigated with the inverse opal films infiltrated with the push-pull type azobenzene polymers.

2. EXPERIMENTAL

2.1. Materials

All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. DcAz2Mc, DR1Mc, and M6PBMe were synthesized according to the manner reported earlier [8–11] and were confirmed by elemental analysis, IR and NMR spectroscopic methods. Synthesis of polymers and copolymers, *poly*(DR1Mc), *poly*(DcAz2Mc), *poly*(DcAz2Mc-*co*-M6PBMe), and *poly*(DR1Mc-*co*-M6PBMe), was carried out by radical polymerization of monomers with the use of *N,N'*-azobis(isobutyronitrile) as initiator at 60°C for 48 hours in dimethylformamide, and their molecular structures are shown in Figure 1. The molecular weights and distributions were measured by gel permeation chromatography (GPC), and the thermal properties were studied by differential scanning calorimetry (DSC).

DR1Mc: m.p. 83°C. Anal. calc. for $C_{17}H_{19}O_2N_2$: C, 62.82; H, 5.80; N, 14.65. Found: C, 62.85; H, 5.80; N, 14.44.

DcAz2Mc: m.p. 135°C. Anal. calc. for $C_{24}H_{23}O_2N_5$: C, 69.88; H, 5.38; N, 16.98. Found: C, 70.00; H, 5.73; N, 16.93.

M6PBMe: m.p. 45°C. Anal. calc. for $C_{24}H_{28}O_6$: C, 66.64; H, 7.23. Found: C, 66.51; H, 7.21.

2.2. Photochemical properties

Photochemical molecular orientation behavior of polymers in the solid state was investigated by using a pump-probe method [4]. Thin solid films were prepared by spin coating method from THF solution. An Ar⁺ laser (LASER GRAPHICS

165 LGS, $\lambda = 488$ nm, 250 mW/cm²) and Xenon lamp (Ushio SX-UI500XQ) equipped with band-pass filter ($\lambda = 500$ –600 nm) were used as a pumping light source, and an He-Ne laser (633 nm) was used as the probe light. The thin solid film of the polymers was placed between two crossed polarizers where the polarizing directions of the polarizers were set at an angle of 45° with respect to the polarizing direction of a pumping laser light. Transmitted light intensity of the He-Ne laser light was measured under irradiation of linearly or circularly polarized Ar⁺ laser light. The photoinduced birefringence, Δn , was estimated [12].

The SiO₂ inverse opal was prepared by the same method described in our previous work [4]. The polymers were infiltrated into the SiO₂ inverse opal film by annealing. Changes in optical properties of the SiO₂ inverse opal/azo-polymer composite films were explored by measuring reflection spectra for incident white light with an Ocean Optics USB2000. Reflection spectra were measured with/without irradiation of Ar⁺ laser or Xenon lamp.

2.3. Calculation

The geometry optimizations of DR1Mc and DcAz2Mc were carried out using Gaussian 98 with B3LYP/6-31G** basis set. Dipole moment, aspect ratio, and polarizability were also calculated with the same level of theory using the standard Gaussian 98 keyword “Polar”. Each birefringence was estimated from polarizability [13].

3. RESULTS AND DISCUSSION

3.1. Photoreponse properties

The cyano group is one of strong electrowithdrawing groups so that side chain type azo polymer having the cyano group, *poly*(DcAz2Mc), was synthesized and its photoresponse behavior was compared with the polymer having DR1 group as the azo-side chains, *poly*(DR1Mc). The molecular weights and glass transition temperatures were 8.8×10^3 and 145°C for *poly*(DcAz2Mc) and 6.1×10^3 and 122°C for *poly*(DR1Mc), respectively, as given in Table 1.

Solid polymer films were prepared by spin coating method. The thickness of the films was estimated spectroscopically, 152 nm for *poly*(DcAz2Mc) and 172 nm for *poly*(DR1Mc), respectively. The photo-orientation behavior was investigated with linearly polarized light irradiation of Ar⁺ laser. The irradiation wavelength of 488 nm is comparable to the absorption band peaks ($\lambda_{max.}$, 465–495 nm) of polymer films as can be seen in Table 1. When the linearly polarized light was irradiated onto the polymer thin films, the uniaxially molecular orientation perpendicularly to the polarization direction of the incident light was confirmed for both films of *poly*(DcAz2Mc) and *poly*(DR1Mc), and the photoinduced birefringences of thin films, Δn , are plotted in Figure 2.

The birefringences of *poly*(DcAz2Mc) and *poly*(DR1Mc) were 0.24 and 0.14, respectively, at the oriented states after prolonged irradiation of linearly polarized light. *Poly*(DcAz2Mc) showed higher birefringence than that of

TABLE 1: Thermal properties and molecular weights of polymers and absorption peaks of their films.

Homopolymers	T_g ($^{\circ}\text{C}$) ^(a)	M_n ^(b)	M_w/M_n ^(b)	λ_{max} (nm) ^(c)	Thickness of films (nm) ^(c)
<i>poly</i> (DR1Mc)	122	6.1×10^3	1.7	465	172
<i>poly</i> (DcAz2Mc)	145	8.8×10^3	1.7	495	152
<i>poly</i> (DR1Mc- <i>co</i> -M6PBMe)	41	1.5×10^4	3.1	485	97
<i>poly</i> (DcAz2Mc- <i>co</i> -M6PBMe)	45	1.2×10^4	3.3	495	100

Determined by DSC^(a), GPC^(b) and UV-absorption^(c).

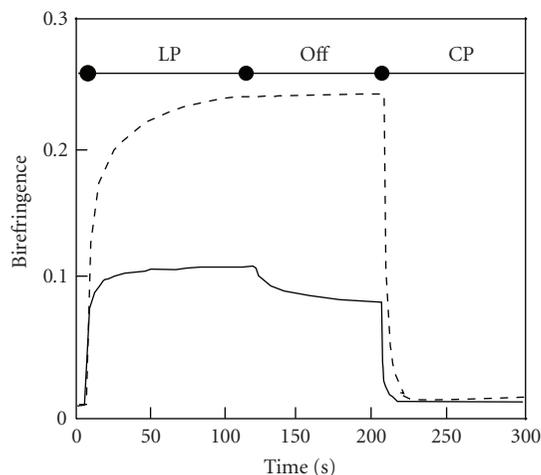


FIGURE 2: Changes in birefringence of *poly*(DR1Mc) (solid line) and *poly*(DcAz2Mc) (dotted line) by irradiation of linearly polarized light (LP) and circularly polarized (CP) light. Ar⁺ laser (488 nm) is used as light source.

poly(DR1Mc). The stability of uniaxial orientation states was also examined under dark condition by monitoring transmitted light intensity after turnoff the irradiation. The oriented state of *poly*(DcAz2Mc) was preserved for hours, while *poly*(DR1Mc) was disordered about 20% within 3 minutes after light off. Thus, it was found that orientation stability for *poly*(DcAz2Mc) film was superior to that of *poly*(DR1Mc). On the other hand, with the irradiation of circular polarized light, the oriented state of both polymers was disordered at once. Based on the experimental results indicating well-controlled photoresponse properties, calculations of geometry optimizations for DR1Mc and DcAz2Mc molecules were computationally carried out in order to explore the relationship between a molecular structure and its orientation behaviors.

3.2. Calculation

The molecular structures and the results of electronic structure calculations for DR1Mc and DcAz2Mc molecules are shown in Figure 3. According to the calculations, the dipole moment values of DcAz2Mc and DR1Mc molecules are 5.31 and 4.08, respectively. DcAz2Mc has larger dipole moment value as 1.23 debye than that of DR1Mc. The result indicates that dicyano electron withdrawing group affords

stronger electronically push-pull property to azobenzene dyes, leading to larger dipole moment. Therefore, it should be expected that DcAz2Mc can undergo more rapid cis-trans isomerization and rapid photoresponse property. On the other hand, the molecular structure geometries are described by the dipole moment distribution and aspect ratio. The dipole moment distributions of both molecules are concentrated along the x -axis of the (x ; y ; z) coordinates in the Gaussian function distribution, and the aspect ratios (L/D) of DcAz2Mc and DR1Mc were, respectively, 2.7 and 2.3. These results indicate that DcAz2Mc molecule has more thin and longish molecular shape than DR1Mc, although both azobenzene dyes are in the rod like molecular shape. In addition, the birefringence of the molecules was calculated from their molecular polarizabilities. A density of 10^3 kg/m^3 and an orientational order parameter S of 0.7 were assumed for the calculation. The birefringences of DcAz2Mc and DR1Mc were 0.58 and 0.43, respectively. Consequently, the photochemically rapid and larger change in the birefringence for DcAz2Mc can be interpreted in terms of the molecular structure geometries and intrinsic optical properties.

3.3. Infiltration of azo polymers into SiO₂ inverse opal

In the procedure of infiltration of polymers into inverse opal, these push-pull type azobenzene polymers were found to have a drawback with their short of fluidity. Since the polymers are generally rigid due to their high T_g and high viscosity compared with low-molar-mass materials. In particular, electronic intermolecular interaction due to push-pull groups substituted in the dyes is considered to attribute to short of fluidity. It brings about a limitation to infiltration into every gap in the inverse opal film or even destroys the silica inverse opal skeleton during cooling down of infiltrated polymers from melted state at high temperature.

In addition, the use of materials containing higher content of azobenzene chromophores may lead to the incomplete photoisomerization over the whole silica inverse opal film infiltrated with the polymers, because of strong absorption of incident light for the photoisomerization near the surface of the inverse opal film. Therefore, in order to induce photoresponse all over the films as well as to provide fluidity, copolymers were synthesized by copolymerization of DcAz2Mc or DR1Mc with M6PBMe for dilution of the content of azobenzene chromophores.

In our study, 5% of push-pull type of azo-group containing polymers, *poly*(DcAz2Mc-*co*-M6PBMe) and *poly*(DR1Mc-*co*-M6PBMe), were prepared by radical

Molecules	Dipole moment	L/D	Δn	Dipole moment distribution for axes		
				x	y	z
DR1Mc	4.08	2.341	0.43	4.05	0.34	0.34
DcAz2Mc	5.31	2.725	0.58	5.25	-0.6	0.55

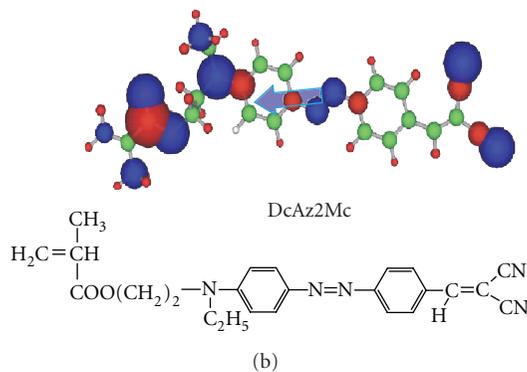
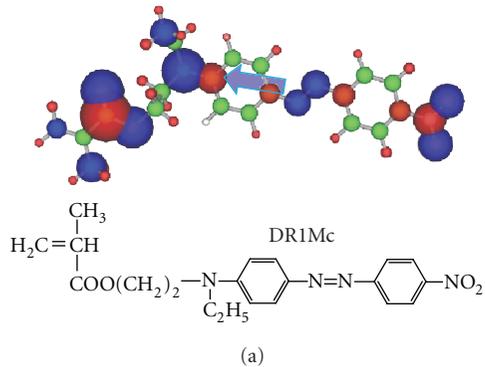


FIGURE 3: Molecular structure designs of DR1Mc and DcAz2Mc and their electronic calculation results of dipole moment distribution, aspect ratio, and birefringence.

polymerization. The structures are shown in Figure 1. T_g of *poly*(DcAz2Mc-co-M6PBMe) and *poly*(DR1Mc-co-M6PBMe) were 45°C and 41°C, respectively, as shown in Table 1. The photo-orientation behavior was investigated with linearly polarized light irradiation with Ar⁺ laser (488 nm). Birefringences of *poly*(DcAz2Mc-co-M6PBMe) and *poly*(DR1Mc-co-M6PBMe) were, respectively, corresponding to 0.11 and 0.09 at the oriented states, as shown in Figure 4. A little content of azo moiety also leads to photo orientation in the copolymer films, and *poly*(DcAz2Mc-co-M6PBMe) shows the higher birefringence than *poly*(DR1Mc-co-M6PBMe).

3.4. Bragg reflection behaviors

The *Poly*(DcAz2Mc-co-M6PBMe) and *poly*(DR1Mc-co-M6PBMe) were readily infiltrated into the inverse opal films by heating to the melting state. Bragg reflection bands of inverse opal films were measured after cooling, and their reflection peaks were observed at 701 nm for *Poly*(DcAz2Mc-co-M6PBMe) and 697 nm for *poly*(DR1Mc-co-M6PBMe), respectively. Change in Bragg reflection band were explored under photo irradiation. When Ar⁺ laser

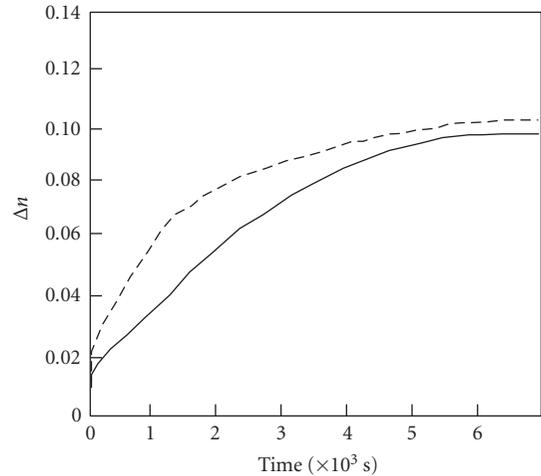


FIGURE 4: Time courses of photo orientation of *poly*(DR1Mc-co-M6PBMe) (solid line) and *poly*(DcAz2Mc-co-M6PBMe) (dotted line) by irradiation of linearly polarized (LP) light. Thicknesses are 172 nm and 152 nm. Ar⁺ laser (488 nm) is used as light source.

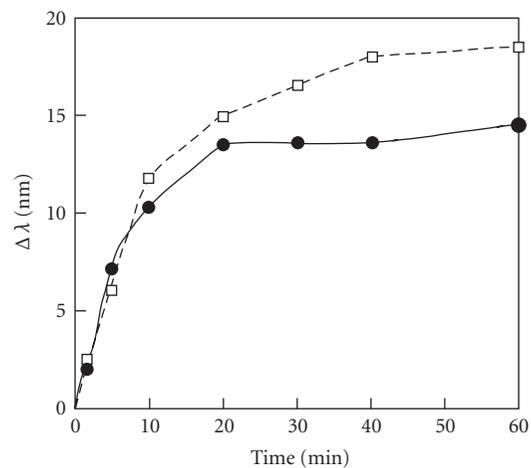


FIGURE 5: Reflection band shifts for *poly*(DR1Mc-co-M6PBMe) (solid line) and *poly*(DcAz2Mc-co-M6PBMe) (dotted line) under linearly polarized light.

was used as light source, no significant change of Bragg reflection band was observed. It is assumed that the narrow wavelength of Ar⁺ laser (488 nm), which is corresponding to the maximum peaks of azobenzene polymers, induces partial photoisomerization only near the surface of the films. In contrast, irradiation of the light with wavelengths ranging from 500 to 600 nm with Xenon lamp was found to cause the change in Bragg reflection band. With linearly polarized light of Xenon lamp (500–600 nm), reflection band peaks of *poly*(DcAz2Mc-co-M6PBMe) and *poly*(DR1Mc-co-M6PBMe) were, respectively, shifted to the longer wavelength region by 18.5 nm and 14.5 nm after irradiation for 1 hour as shown in Figure 5.

4. CONCLUSION

DR1Mc and DcAz2Mc, having push-pull type of azobenzene group, are prepared and their photo-orientational behaviors are compared. It is found that DcAz2Mc molecule is theoretically and experimentally advantageous structure for rapid photo response and orientation behavior than that of DR1Mc. In the inverse opal films infiltrated with their copolymers, Bragg reflection bands are shifted to the longer wavelength region under irradiation of linearly polarized light. The shift width for *poly*(DcAz2Mc-co-M6PBMe) is larger than that for *poly*(DR1Mc-co-M6PBMe).

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